IL NUOVO CIMENTO Vol. 35 C, N. 5 Settembre-Ottobre 2012
DOI 10.1393/ncc/i2012-11310-x

Communications: SIF Congress 2011

Multiferroic and magnetoelectric metal-organic frameworks

A. Stroppa(*)
CNR-SPIN - L'Aquila (AQ), Italy

ricevuto il 24 Gennaio 2012; approvato l' 1 Febbraio 2012

Summary. — We present an *ab initio* study of the $[C(NH_2)_3][Cu(HCOO)_3]$ compound. It belongs to a new class of multifunctional materials, namely multiferroic metal-organic frameworks. We show that this compound is multiferroic, with coexistence of ferroelectricity and magnetism. Furthermore, it is also magnetoelectric. Our study suggests that multiferroic metal-organic frameworks are a very promising class of materials.

PACS 75.85.+t – Magnetoelectric effects, multiferroics.
PACS 77.55.Nv – Multiferroic/magnetoelectric films.
PACS 33.15.Fm – Bond strengths, dissociation energies.
PACS 75.30.Kz – Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.

1. – Introduction

Multiferroics are materials which show at least two coexisting ferroic orders in a single phase [1] like for instance, ferroelectric and magnetic orders. They are potential applications in future magnetic data storage and spintronic devices [2-8] provided a simple and fast way can be found to turn their electric and magnetic properties on and off. They can be applied as high-sensitivity ac magnetic field sensors and electrically tunable microwave devices such as filters, oscillators and phase shifters [9]. A special case is when both orders are coupled, thus allowing a cross-coupling where one can tune the ferroelectric response by a magnetic field, and vice versa, one can tune the magnetic response by an applied electric field [9].

There is a great interest in the literature about multiferroic and magnetoelectric materials. By a simple search in ISI WEB of Science, using keywords such as "multiferroic* OR magnetoelectric*" as topic, one gets a list of almost 1000 papers published in 2011 giving an overall h-index of 97 cumulated over the years. However, most of these studies

(*) E-mail: alessandro.stroppa@aquila.infn.it

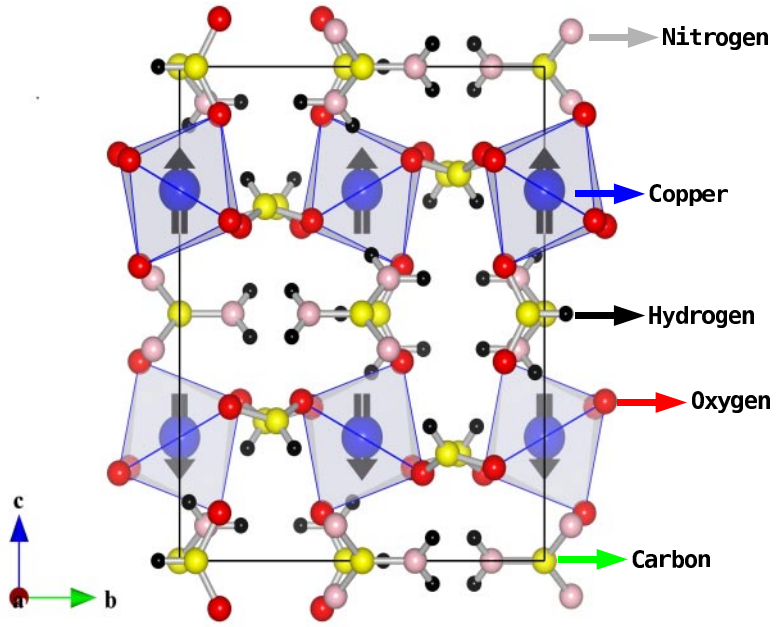

Fig. 1. – Crystal structure of the Cu-MOF. One can see the octahedra linked by HCOO groups, and the A-site of the perovskite network occupied by $C(NH_2)_3$ groups. For more details, we refer to ref. [25] The spin configuration is represented by arrows at Cu sites.

deal with inorganic compounds, mainly complex oxides derived from the perovskite-type family. Only very recently, new directions started to emerge, shifting the focus towards organic or hybrid organic-inorganic materials [10]. A pioneering paper along this line is the work by Jain *et al.* [11-14], where they show multiferroic behavior associated with an order-disorder hydrogen bonding transition in metal-organic frameworks (MOFs) with perovskite ABX_3 architecture. The search of multiferroicity in MOFs is a very attractive emerging route already showing promising potential results [15, 16].

MOFs are crystalline hybrid materials containing both inorganic and organic components. They are very attractive materials for gas storage, drug delivery, catalysis, optics and magnetism [17-19]. Essentially, the MOF structure is made up of a framework of metal ions coordinated by organic ligands and forming a porous framework, whose cavities can be filled by molecular ions. An interesting class of MOF has recently attracted great attention. It has a ABX_3 perovskite topology, where A is an organic cation, B is a transition metal, X is an organic ligand. These compounds provide access to more oxide-like properties, like for instance, multiferroicity [20-24].

2. – Cu-MOF

In this framework, we have studied by *ab initio* calculations the $[C(NH_2)_3][Cu(HCOO)_3]$ MOF (hereafter called Cu-MOF), where the A group is the guanidinium cation $C(NH_2)_3{}^+$, B is Cu^{+2} and X is $HCOO^-$. Details of the computational parameters can be found in ref. [25] In fig. 1 we show a side view of the compound. It is easy to recognize the octahedra connected by carboxylic ligands and the guanidinium cation which fill the A-site of the perovskite topology.

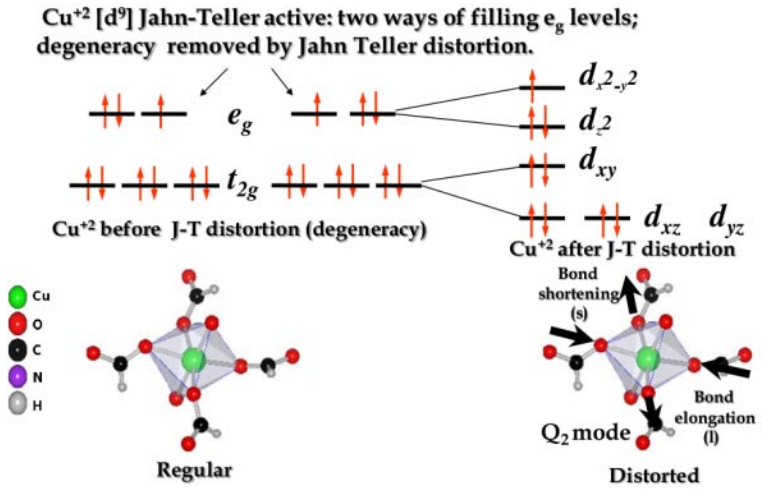

Fig. 2. – Electronic degeneracy removed by Jahn-Teller distortions through the Q_2 mode.

An important feature in this compound is the presence of Jahn-Teller active Cu^{+2} ions, having a d^9 electronic configuration. The degeneracy of this configuration is removed by an octahedra structural distortion, which, in turns, introduces *long* and *short* Cu-O bonds in the *ab* basal plane (Q_2 Jahn-Teller mode). A schematic summary is presented in fig. 2.

The different orientations of the *long* Cu-O bonds on different Cu sites give rise to a characteristic anti-ferrodistortive pattern: the *long* Cu-O bond on one Cu site is almost perpendicular to the *long* Cu-O bond on neighboring Cu site. One can introduce a function through the definition of a parameter ϕ. This parameter is an effective angle which quantifies the "degree" of antiferro-distortion (AFD): for $\phi = 4\pi/3$ or $2\pi/3$, one has a maximum distortion in our system, while for $\phi = \pi$, one has that Cu-O *long* and *short* bonds are equal. It must be noted that AFD modes are usually non-polar in standard inorganic ABX_3 compounds. We will come back to this point shortly.

The ground state is antiferromagnetic, with Cu spins ferromagnetically coupled within the *ab* plane while antiferromagnetically coupled between parallel *ab* planes (see fig. 1). Note that, by introducing the spin-orbit coupling in the calculations, a weak ferromagnetic component appears, *i.e.* the spins are tilted. This will have important consequences for the magnetoelectric behavior in this compound (see ref. [25]). It is important to stress that the Cu-MOF crystallizes in a polar space group, $Pna2_1$ [23]. Therefore, the magnetic ground state in a polar space group suggests a possible multiferroic behavior. In order to explore this possibility we have introduced a virtual paraelectric (centric) structure by using the PSEUDOSYMMETRY tool [26]. This virtual paraelectric structure has $Pnan$ space group. In this way, one can present the crystal structure as due to symmetry-lowering structural distortion from the high-symmetry centric group. It is useful to introduce a parameter λ which is proportional to the amplitude of the polar distortion connecting the centric to the polar structure: $\lambda = 1$ represents the compound in the $Pna2_1$ space group, $\lambda = 0$ represents the $Pnan$ centric space group. For each $\lambda \in (0, 1)$, one can linearly interpolate between the two end-points, defining a continuous path as a function of λ. Obviously, one can also consider the $\lambda = -1$: this state has again $Pna2_1$ space group symmetry, but the polarization has been reversed with respect to $\lambda = 1$.

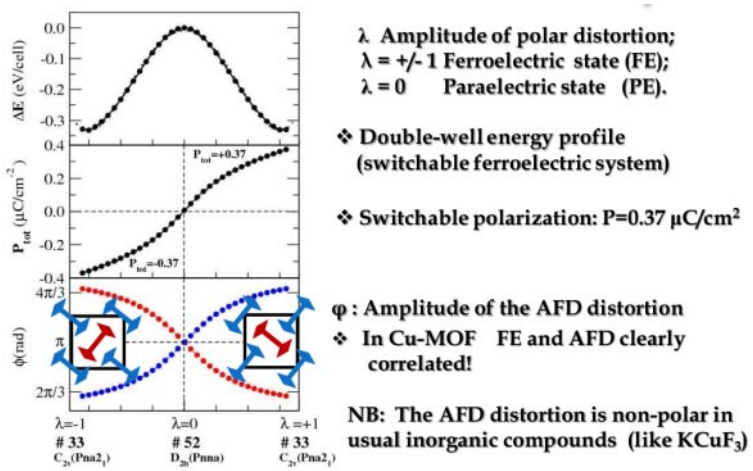

Fig. 3. – Energy, polarization and AFD distortion along the path connecting the virtual paraelectric structure and the polar ones. The insets show the orientations of the *long* Cu-O bonds of the two Cu sub-lattices.

We found that at $\lambda = \pm 1$, the system has a finite polarization $P = 0.37\,\mu\mathrm{C/cm^2}$. As expected, at $\lambda = 0$, $P = 0$. It turns out that $P = P(\lambda)$ is a monotonically increasing odd function of the polar distortion. The calculated energy profile as a function of λ produces the expected double-well profile characteristic of a switchable ferroelectric system. Surprisingly, by monitoring the changes of ϕ along the path, we have found a clear correlation between $P = P(\lambda)$ and $\phi(\lambda)$. In principle, one has $\phi_{\alpha,\beta}(\lambda)$, where α, β denotes the two Cu-sublattice in the ab plane. Each sublattice has the same orientation of the *long* Cu-O bonds, but the orientation "rotates" by 90 degrees in the neighboring Cu site. One can see that $P = P(\lambda)$ and $\phi(\lambda)$ have the same behavior as a function of λ, thus suggesting that AFD distortions can be the source of the ferroelectric polarization. In fig. 3 we show the energy E, the polarization P, and the "amplitude" of the AFD distortions along the path.

The microscopic explanation of the ferroelectric polarization and its relation to AFD modes have been discussed in details in ref. [25] Here we remind the main ideas. The $[C(NH_2)_3]^+$ molecular group interacts with the BX_3 framework through hydrogen bonding $N{-}H\cdots O$, where the first H belong to NH_2 of the $[C(NH_2)_3]^+$ group, and the O is bond to Cu. Both the H atoms of the NH_2 group feel the H bonding, but while at the $\lambda = 0$ state, the H bonding strength is the same, for λ larger than 0, *i.e.* towards the ferroelectric state, the H bonding strength becomes asymmetric for the two H atoms, due to the crystalline environment [25]. Since the AFD mode basically controls the oxygen positions, the change of the AFD mode amplitude (changing ϕ along λ), induces asymmetric distortions in the NH_2 part of the A-group, *i.e.* there is an induced dipole moment which then sums up to give a finite polarization. This explains the microscopic origin of the ferroelectric polarization in this compound.

3. – Conclusion

We have shown that the Cu-MOF, belonging to the metal-organic framework family with ABX_3 topology, shows a rich and fascinating physics. Our study supports the following picture: i) It is ferroelectric with an estimated polarization of $0.37\,\mu\mathrm{C/cm^2}$.

ii) The origin of the ferroelectricity is very intriguing: nonpolar distortions (*i.e.* antiferrodistortions) give rise to a loss of inversion symmetry, paving the way for the appearance of polarization; note that this mechanism is not found in classical ABX_3 inorganic compounds. iii) Hydrogen bonding plays a major role in coupling the nonpolar distortions acting in the BX_3 framework with the organic cation. iv) A weak ferromagnetic component is allowed and it is coupled to the ferroelectricity: by using this very rare property, it would be possible to control the polarization by an applied magnetic field, and vice versa. This is called magnetoelectricity. This feature has not been discussed here, but we refer to ref. [25] for more details.

* * *

This research was funded by the European Research Council under the European Community, 7th Framework Programme (2007–2013)/ERC Grant Agreement no. 203523 won by Dr. S. Picozzi. Computational support by CASPUR Supercomputing Center in Rome through Standard HPC Grant 2010 is gratefully acknowledged. Figures were plotted using the VESTA package [27].

REFERENCES

[1] Schmid H., *Ferroelectrics*, **162** (1994) 317.
[2] Bibes M. *et al.*, *IEEE Trans. Electron Dev.*, **54** (2007) 1003.
[3] Gajek M. *et al.*, *J. Appl. Phys.*, **97** (2005) 103909.
[4] Gajek M. *et al.*, *Phys. Rev. B*, **72** (2005) 020406(R).
[5] Gajek M. *et al.*, *Nat. Mater.*, **6** (2007) 296.
[6] Stroppa A. *et al.*, *Phys. Rev. B*, **75** (2007) 195335.
[7] Wu H. *et al.*, *Phys. Rev. Lett.*, **105** (2010) 267203.
[8] Stroppa A. *et al.*, *Phys. Rev. B*, **77** (2008) 035208.
[9] Nan C. W. *et al.*, *J. App. Phys.*, **103** (2008) 031101.
[10] Kagawa F. *et al.*, *Nature Phys.*, **6** (2010) 169.
[11] Jain P. *et al.*, *J. Am. Chem. Soc.*, **130** (2008) 10450.
[12] Jain P. *et al.*, *J. Am. Chem. Soc.*, **131** (2009) 13625.
[13] Baker P. *et al.*, *Phys. Rev. B*, **82** (2010) 012407.
[14] Jain P. *et al.*, *Proc. Natl. Acad. Sci. USA*, **108** (2011) 6828.
[15] Ramesh R., *Nature*, **461** (2009) 1218.
[16] Rogez G., *Angew. Chem. Int. Ed.*, **49** (2010) 1821.
[17] Yaghi O. M. *et al.*, *Nature*, **423** (2003) 705.
[18] Férey G. *et al.*, *Science*, **283** (1999) 1125.
[19] Rao C. N. R. *et al.*, *J. Phys.: Condens. Matter*, **20** (2008) 083202.
[20] Cheetham A. K., *Science*, **318** (2007) 58.
[21] Férey G. *et al.*, *Chem. Soc. Rev.*, **37** (2008) 191.
[22] Wang X. Y. *et al.*, *Inorg. Chem.*, **43** (2004) 4615.
[23] Ke-Li H. *et al.*, *Chem. Eur. J.*, **15** (2009) 12050.
[24] Clausen H. F. *et al.*, *J. Solid State Chem.*, **178** (2005) 3342.
[25] Stroppa A. *et al.*, *Angew. Chem. Int. Ed.*, **50** (2011) 5847.
[26] Capillas C. *et al.*, *Z. Krist.*, **226** (2011) 186.
[27] Momma K. *et al.*, *J. Appl. Crystallogr.*, **41** (2008) 653.